OFFICIAL DOCUMENT

Albuquerque Bernalillo County
Water Utility Authority

WATER RECLAMATION DIVISION
4201 2ND STREET SW, ALBUQUERQUE, NEW MEXICO 87105

WATER QUALITY LABORATORY
STANDARD OPERATING PROCEDURE APPROVAL FORM

WQL SOP 504
Metals by Graphite Furnace Atomic Absorption

CURRENT REVISION # 05 DATE: February 28, 2008

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MODIFICATIONS AND REASONS FOR REVISION

*Purchase of AAnalyst 800 in 3/23/2006
*Purchase of two AAnalyst600 in 12/27/2006
*New SOP format
*New hire to Management Staff

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History of Revision This table lists the revision history and effective dates of this procedure.

Revision	Date	Description of Changes
01	2/1/1988	New Instrument and New Method Development
02	2/1/1988	Information not available
03	2/1/1996	A2LA Accreditation Requirement
04	7/21/2004	A2LA Requirement for SOP Approval Form
05	2/22/2008	Purchase of AAnalyst 800 and two AAanlyst 600 New SOP Format New hire to Management Staff

1.0 SCOPE AND APPLICATION

1.1. This standard operating procedure is applicable to the determination of silver, cadmium, chromium, arsenic, lead, antimony, selenium, and thallium in drinking water, surface and saline waters, and domestic and industrial wastes.

2.0 SUMMARY OF METHOD

2.1. **Spectrometer**- The spectrometer provides a means of measuring light at a specific wavelength. To provide this function, the spectrometer uses a primary light source, a monochromator, and a detector. The primary light source, either a hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL) is placed in the spectrometer to emit the narrow atomic lines of the element to be determined. The light passes through the sample compartment and is absorbed by the atomized sample. The monochromator disperses the various wavelengths of light and isolates the particular line of interest. The light leaving the monochromator is directed onto the detector, a photomultiplier tube (PMT), which produces an electrical signal proportional to the light intensity. The electrical signal is amplified and processed to produce a signal which is a measure of the light attenuation occurring in the sample compartment.

2.2. **Graphite Furnace Atomic Absorption (GFAA) Principle**- AA spectroscopy requires that the analyte atoms be in the gas phase. Ions or atoms in a sample must undergo desolvation and vaporization in a high-temperature source such as a flame or graphite furnace. In GFAA, sample is introduced directly into the electrically heated graphite tube, which is then heated in a programmed series of steps to remove the solvent and major matrix components. The remaining sample undergoes complete atomization. The atomized sample is retained within the tube/light path for an extended period of time (The light path passes though the tube). As a result, sensitivity and detection limits are enhanced.

2.3. **Perkin-Elmer Graphite Furnace**- Consists of a furnace and power supply. The sample is placed inside the THGA graphite tube and the tube is electrically heated to atomize the sample. A continuous flow of inert gas inside and outside the tube protects the tube from air oxidation and flushes out the gaseous products. A re-circulating water cooling system maintains the furnace at a specified temperature and to cool it between analyses. Operating parameters, including a furnace program, are entered and stored in the computer and then implemented during analysis.

2.4. **Zeeman Furnace Module**- The Zeeman furnace provides Zeeman-effect background correction for the graphite furnace sampling technique. Spectrometer optics are coupled with the optical components in the Zeeman module via an optical interface. (*PE THGA Graphite Furnace Techniques and Recommended Conditions* pp. 2-9 – 2-16).

2.5. **Optics**- The AA600 and AA800 spectrometers include an optical system optimized for Zeeman sampling through the optical interface on the left-hand side of the instrument. Note: The monochromator isolates the wavelength of interest before allowing the light to fall on the photomultiplier. The correct grating is chosen and its angle is set automatically by the software.

3.0 DEFINITION OF TERMS

3.1. **QA SOP-007**- Reference for general terms related to quality and technical procedures, which applies to all standard operating procedures within WQL.

3.2. **Matrix Modifier**- Reduces analyte volatility, increases matrix volatility, and reduces background absorption.

3.3. **Peak Absorbance**- The highest absorbance signal of an absorbance peak profile.

3.4. **Pretreatment Step**- Used to condition the sample before atomization by ashing or volatilizing the matrix. This step is also referred to as the char step.

3.5. **Rollover-** A decrease in absorbance signal at the center of a peak profile at higher analyte concentrations. Rollover occurs with Zeeman background correction.

3.6. **Volatilization-** Passing from a solid or liquid state to a vapor.

3.7. **Zeeman-** A background correction system based on the splitting of an atomic spectral line in a magnetic field.

4.0 INTERFERENCES

4.1. **Background Interferences-** Some samples, when atomized, may absorb or scatter radiation from the source because, simultaneous with atomization, components of the sample matrix also volatilize. The volatilized sample matrix may exist as a gaseous molecule species, salt particles, smoke, or other phenomenon. The combined effect is known as Background Absorption. An absorption signal can become masked or enhanced by the volatilized matrix and may be mistaken for the analyte signal. Background interference effects may be more pronounced at shorter wavelengths. Since background absorption is less specific and extends over a considerably broader wavelength band it usually can be distinguished from analyte absorption; in which an element only absorbs the very narrow spectral line emitted by the source. In summation, Background Interference is non-specific, results in a false high and is caused by light scattering and molecular absorbance

The Background Corrector is an instrumental method used to correct background absorption effects. Simultaneous compensation is obtained at the same wavelength used to measure atomic (elemental) absorption. Radiation from the source lamp and a corrector lamp are passed alternately through the graphite furnace. The element being determined effectively absorbs only light from the source lamp, while background absorption affects both beams equally. When the ratio of the two beams is taken electronically, the effect of background absorption is eliminated.

To control spectral interferences due to background absorption, continuum source or Zeeman-effect background correction is used. Continuum source background correction uses a deuterium lamp light source that emits light over a broad spectrum of wavelengths. Zeeman-effect background correction is based on the splitting of the atomic absorption line in a magnetic field profile into three or more polarized components.

4.2. **Chemical Interferences-** The most common interferences in atomic absorption are chemical interferences. Their effects can be minimized by a suitable choice of operating conditions. These interferences can be categorized as: 1) formation of compounds of low volatility which reduce the rate at which the sample is atomized, 2) ionization of atoms and molecules, and 3) solute vaporization effects. These interferences can be minimized by varying the temperature and addition of an ionization suppressor or by standard addition technique.

4.3. **Physical Interferences-** Physical interferences are pronounced with samples containing high dissolved solids and/or acid concentration resulting in change in viscosity and surface tension. If these types of interferences are operative, they can be reduced by diluting the sample.

4.4. **Matrix Interferences-** Matrix interferences can cause either a suppression or enhancement of the analyte signal. Matrix interferences occur when the physical characteristics (viscosity, burning characteristics, surface tension, etc.) of the sample and standard differ considerably. This can happen when the sample solution contains a high concentration of dissolved salts or acid, when different solvents are used for sample and standard solutions, or when the sample and standard solutions are at radically different temperatures.

To compensate for matrix interferences, closely match the matrix components in the sample, standard, and blank. Any reagent added to the samples during preparation should also be added to the standards and the blank. In addition Matrix modifiers are used to stabilize analyte and volatilize matrix (get rid of salts at lower temperatures). Example of matrix volatilization:

$$NaCl + NH4NO3 \rightarrow NaNO3 + NH4Cl.$$

5.0 SAFETY

5.1. Health Hazards

5.1.1. For specific hazards, consult the MSDS for compounds listed in section 7.0 of this SOP [MSDS on file in WQL Conference Room].

5.1.2. Use, store, and dispose of chemicals in accordance with WQL Chemical Hygiene Plan (CHP-Section 5- Revision December 2005). All wastes generated by this procedure must be disposed of in an acid waste sink.

5.1.3. The furnace system is capable of generating high temperatures for atomization. The icon in the HGA Control Window will indicate when the furnace is cooled down after a heating cycle. The THGA graphite furnace can generate temperatures up to 2600 C. Do not touch any part of the graphite furnace until it has cooled down to room temperature. Do not attempt to inject a sample into the graphite tube when the furnace is hot. You may be subjected to fumes from the sudden vaporization of the sample, and may damage the pipette.

5.2. Protective Equipment

5.2.1. Wear appropriate Personal Protective Equipment (PPE) in accordance with WQL CHP (Section 5.1 – Revision December 2005).

5.2.2. **Warning:** Never directly view the furnace during the atomization step, the hollow cathode lamps or electrodeless discharge lamps without protective eyewear.

5.3. Spills and Contamination

5.3.1. Clean up spills immediately in accordance with WQL CHP (Section 5.11-Revision December 2005).

5.3.2. Conduct sample preparation away from the instrument to minimize corrosion and contamination

5.4. **Waste Bottles-** Waste bottles must be maintained to provide safe operation. Place the polyethylene (PE) waste bottle in plain sight of the operator (i.e. on floor, in front of the instrument.). Do not use plastic or metal containers. Check the condition of the drain tubing regularly for deterioration. Replace as needed. Frequently empty the waste bottle. As described in Section 5.1.2.

5.5. **Exhaust Ventilation-** A venting system is required to remove the fumes and vapors from atomic absorption instruments. Exhaust Ventilation protects the instrument and laboratory personnel from toxic and corrosive vapors and also aids in removing the effects of room drafts in the laboratory atmosphere. Vents are checked monthly by Chemical Hygiene Officers. Notify a supervisor immediately if an exhaust vent is not operating properly!

5.6. **Safety Interlocks-** The graphite furnace has a safety interlock that checks the condition of the graphite tube for breakage. Additional interlocks check that the furnace is properly cooled, monitor argon pressure, and monitor the temperature of the power supplies. All interlocks must be satisfied before you can operate the system.

5.7. Handling/Storing High Pressure Gas Cylinders and Dewars

5.7.1. Gas cylinders are stored in the gas storage room; ensure that ventilation is adequate to prevent toxic or explosive accumulations of gas.

5.7.2. Do not allow ignition sources in the storage area and keep cylinders away from readily ignitable substances such as gasoline or waste.

5.7.3. Store all gas cylinders only in a vertical position, with the value cap in place, and fastened securely to an immovable bulkhead.

5.7.4. When transporting a cryogenic liquid container (dewar) of argon or other gasses, use a hand truck specifically designed to fit the dewar.

5.7.5. Ask for help if you feel you need help with transporting a gas cylinder.

5.8. **Magnetic Field-** The Furnace generates a strong magnetic field during measurement cycles. Do not operate the furnace when persons wearing heart pacemakers or other metallic implants are present.

5.9. **Safety Checks-** Daily check that the vent is on and drawing properly and that the inert gas supply is connected and set to the correct pressure.

6.0 APPARATUS AND EQUIPMENT

6.1. All analytical equipment requirements for availability, installation, out-of-service, and record keeping (identification, manufacture, serial #, model #, and date of purchase) will follow WQL Quality Assurance Manual (QAM) procedures (Section 5.5).

6.2. **AAnalyst 600 atomic absorption spectrometer or AAnalyst 800 atomic absorption spectrometer-** Contain the optical system, the electronics, and the atomizer compartment. The spectrometers consist of five basic components (Refer to *AA600 Users Guide*, section 5-3 for parts and supplies provided, replacement parts, and accessories) :

1. Light source- emits the spectrum of the element of interest.
2. Absorption cell – furnace where atoms of the sample are produced.
3. Monochromator- disperses light
4. Detector- measures the light intensity and amplifies the signal
5. Display- shows the reading after it has been processed by the instrument electronics

The AAnalyst 800 has two fully integrated atomizers: a burner system for flame atomization and a graphite furnace for electro thermal atomization. The graphite furnace is mounted on a carriage that can be driven into and out of the atomizer compartment by software command (Refer to Furnace Design, pg. 5-3, in the Graphite Furnace Users Guide). The AAnalyst 600 lacks a flame atomization burner system

6.3. **AS-800 Furnace Autosampler-** Mounted on a swing arm, in front of the atomizer compartment, the AS 800 contains 88 sample cups and is powered by the THGA Power Unit and controlled by the computer. Once the tray is loaded, the sample is automatically pipetted using a probe placed in a mechanically operated sampling arm. Some of the automatic features you can perform using an autosampler include:

1. Rinsing between samples
2. Running standards to calibrate and recalibrate the instrument
3. Running check samples to check instrument performance
4. Introducing a matrix modifier into the graphite furnace

6.4. **Computer System-** The computer controls the hardware components and collects, processes, and stores the analytical data. The computer processes the signals received from the spectrometer to produce a readout of sample concentration.

6.5. **Inert Gas-** The graphite furnace requires a supply of inert gas to prevent the tube and the analyte atoms from being oxidized when the tube is heated. A high purity, high pressure Argon is required.

6.6. **Cooling System-** A re-circulating water cooling system (1:10 solution of glycerol in distilled water) provides coolant at a constant temperature and flow. The AA600 is connected to a Perkin Elmer AAAccessory Cooling System and the AA800 is connected to a Perkin Elmer Furnace Cooling System. Refer to the PE Cooling System User's Guide for maintenance and operating conditions. Cooling coils are also incorporated in the spectrometer's power supply to maintain the lectronic components at a comfortable working temperature (PE AAnalyst 600 Users Guide, pg. 6-14).

6.7. **Lamps-** Hollow cathode lamps (HCL) and electrodeless discharge lamps (EDL) are used. EDL's provide greater intensity than the HCL's. NOTE: EDLs lack the integral element identification plug that fits into the socket under the lamp. This insert identifies the lamp to the software. Use a separate (element specific) plug that identifies the lamp to the software when utilizing EDL lamps for furnace analysis.

6.8. **Glassware-** Class A volumetric flasks

6.9. **Calibrated pipettes-** Class A

6.10. **Sample Cups-** 2 mL polystyrene & 7 mL polypropylene, metal free cups

7.0 REAGENTS AND STANDARDS

7.1. **Chemicals/Reagents** - All chemicals and reagents transport and storage requirements will follow WQL QAM procedures (Section 5.6.4).

7.2. **Filtered Deionized Water-** Use to prepare 1 % HNO3.

7.3. **Argon-** A supply of inert gas is required for external and internal gas streams through the graphite furnace. Argon with a purity criterion of ≥ 99.996% is required.

7.4. **1% HNO_3-** Use 1% HNO_3 for the preparation of all reagents, calibration standards, rinse samples during analysis, Auto Zero blank sample, rinse vessel and as dilution water.

7.5. **Initial Calibration Standards (ICAL) -** Prepare standard metal solutions in concentration ranges listed below. Follow method procedures in Table 1. Record *date prepared*, *source/inventory number*, *analyst*, *expiration date*, and *reference #* in *Furnace Standards Logbook* (See section 15.0).

		S1	S2	S3
1.	Ag:	2.5 µg/L	5 µg/L	10 µg/L
2.	As/Pb/Se/Sb/Tl:	10 µg/L	25 µg/L	50 µg/L
3.	Cd:	0.5 µg/L	1.0 µg/L	2.0 µg/L
4.	Cr:	2 µg/L	10 µg/L	20 µg/L

Table 1. Furnace ICAL Preparation Methods

ICAL Stocks/Standards	Preparation Method
1ppm Stock Ag	0.5mL PE N930-0151→ 500mL 1% HNO_3
2.5µg/L Ag	5mL 5ppb Ag + 5mL 1% HNO_3
5µg/L Ag	0.25mL 1ppm Stock → 50mL 1% HNO_3
10µg/L Ag	0.5mL 1ppm Stock → 50mL 1% HNO_3
1ppm Stock As/Cd/Cr/Pb/Sb/Se/Tl	5mL PE N930-0281 → 500mL 1% HNO_3
0.5µg/L Cd	5mL 1ppb Cd + 5mL 1% HNO_3
1µg/L Cd	0.05mL PE N9300281 1ppm Stock → 50mL 1% HNO_3

2µg/L Cd/Cr	0.1mL PE N9300281 1ppm Stock → 50mL 1% HNO_3
10 µg/L Cr/Pb/Se/As/Sb/Tl	0.5mL PE N9300281 1ppm Stock → 5mL 1% HNO_3
20 µg/L Cr	1mL PE N9300281 Stock → 50mL 1% HNO_3
25µg/L As/Pb/Se/Sb/Tl	1.25mL PE N9300281 1ppm Stock → 50mL 1% HNO_3
50µg/L As/Pb/Se/Sb/Tl	2.5mL PE N9300281 1ppm Stock → 50mL 1% HNO_3

7.6. **Initial Calibration Verification Standard (ICVS) -** Reference QA SOP 005. Follow method procedures in Table 2. Record *date prepared*, *source/inventory number*, *analyst*, *expiration date*, and *reference #* in *Furnace Standards Logbook.*

1. As/Pb/Se/Sb/Tl ICVS 25 µg/L
2. Cd ICVS 1.0 µg/L
3. Cr ICVS 10.0 µg/L
4. Ag ICVS 5.0 µg/L

Table 2. Furnace ICVS Preparation Methods

ICVS Stocks/Standards	Preparation Method
1ppm Stock As/Pb/Cr/Cd/Se	1mL RICCA Cat.No. RTRACE 1-100 → 100mL 1% HNO_3
25 µg/L As/Pb	1.25mL RICCA RTRACE 1-100 1ppm Stock → 50mL 1% HNO_3
10µg/L Cr	0.5mL RICCA RTRACE 1-100 1ppm Stock → 50mL 1% HNO_3
25µg/L Se	5mL RICCA RTRACE 1-100 1ppm Stock → 50mL 1% HNO_3
1µg/L Cd	0.2mL RICCA RTRACE 1-100 1ppm Stock → 50mL 1% HNO_3
0.5ppm Stock Ag	0.05mL JT Baker 5779-04 → 100mL 1% HNO_3
5µg/L Ag	0.5mL JT Baker 5779 0.5ppm Stock → 50mL 1% HNO_3
1ppm Sb/Tl Stock	1mL PE N9300244 → 100mL 1%HNO_3
25µg/L Sb/Tl	1.25mL PE N9300244 1ppm Stock→ 50mL 1%HNO_3

7.7. **Continuing Calibrations Verification Standard (CCVS) -** Calibration Standard 2 will be used as CCVS to verify instrument performance.

7.8. **Matrix Modifiers**- Matrix modifiers should be prepared as noted, with all pertinent information recorded in the Furnace Standards log book.

1. **Ag, As, Sb, Se & Tl** – 3 mL Pd $(NO_3)_2$ stock (PE # B0190635) + 300µl $Mg(NO_3)_2$ stock (PE #B0190634) diluted to 10mL with 1% HNO_3.

2. **Cd, Pb** – 40g $NH_4H_2PO_4$ stock (PE #N930-3445) + 2g Mg $(NO_3)_2$ stock (PE #B0190634) diluted to 1L with 1% HNO_3.

3. **Cr** – 1.7mL Mg $(NO_3)_2$ stock (PE #B0190634) to 10mL with 1% HNO_3.

8.0 QUALITY ASSURANCE/ QUALITY CONTROL

8.1. **Analyst Training** - Analysts must follow the steps outlined in the DOC Training Program for WQL SOP's. Follow requirements in QA SOP-004.

8.2. **Quality Control Requirements** – Follow requirements in QA SOP-005. The Quality Control Requirements section covers the following topics: 1) Quality Control Limits 2) Quality Control - Instrument Performance 3) Laboratory (Method).

8.3. **Data Evaluation**- Follow requirements in QA SOP-005. The Data Evaluation section covers the following topics: 1) Internal Audits 2) Control Charts Procedures 3) Performance Audits 4)

Method Detection Limit Procedures (See section 15.0 for *Furnace Instrument and Sample Control Data Logbook* and *Furnace MDL Verification* document).

8.4. **Chemicals/Reagents/Gases-** All chemicals and reagents used will be assigned a WQL reference number and a Certificate of Analysis will be filed in the WQL QA file room. Ultra Pure chemicals and Ultra High Purity gases are used for all metals analyses. Label all reagents with the date received, date opened, and the analyst's initials.

8.5. **Equipment Preventive Maintenance Procedure-** Maintenance procedures are recorded in the *Maintenance, Repair, and Corrective Actions Logbook* (See section 15.0). The analyst is responsible to perform and record the specified duties listed in the *Maintenance Log* on a routine basis and to fill out the *Repair Log* when any repairs are made. The analyst must ensure that the Perkin-Elmer Technician, at time of service, completes the *Repair Log* and *Maintenance Log*. File all Perkin-Elmer service report copies in the QA file room. It is the responsibility of the supervisor to order the service reports from Perkin-Elmer for each maintenance visit.

8.6. **HNO_3 Testing-** Analyze a HNO_3 blank with every new lot of HNO_3 prior to usage in order to eliminate any possible HNO_3 contamination. Record in the *HNO_3 Logbook* (See section 15.0).

8.7. **Furnace Standards Logbook-** Record all standards and Matrix Modifiers in the *Furnace Standards Logbook* (See section 15.0). The logbook provides a method for standard preparation which includes the stock standard and vendor, the volume used, and the total volume prepared ($C_IV_I = C_FV_F$). Record the *Date Prepared*, *Analyst Initials*, *Source/Inventory #*, *Expiration Date*, and *Reference #* in the Logbook. Record any deviations in the *Comments* column. The reference number corresponds to the page number and date analyzed of the specific standard (i.e. 22-091508, 22 reflects the page number and 091508 reflects the date prepared, September 15, 2008).

Label the container of the specific prepared standard with the reference number, expiration date and analyst initials. This allows the analyst to cross reference any standard in the laboratory.

Note: All furnace standards have a two (2) week shelf life.

8.8. **Instrument Quality Control-** To eliminate sample contamination, ensure that the reservoir bottle always contains sufficient 1% HNO_3 and follow all maintenance procedures to eliminate contamination.

8.9. **Contamination-** The detection limits attainable with the graphite furnace are affected by the amount of contamination present. Avoid inorganic contamination of glassware by following the glassware preparation procedure in the *Sample Preparation SOP 501*, section 6.2.

9.0 PROCEDURE

9.1. **Sample Handling**

9.1.1. **Preservation** - Samples are collected in polypropylene or polyethylene containers and are preserved by acidifying with concentrated HNO_3 to pH <2. Dissolved metals samples are filtered prior to preservation.

9.1.2. **Sample Holding Time** – Sample holding time is 6 months for metal analyses.

9.1.3. **Storage** – Un-prepared and prepared samples are stored at room temperature in designated Metals Storage Area. Samples that may have legal ramifications due to regulatory incompliance limits are to be stored in a secure area but for no longer than their allowed holding times.

9.1.4. **Sample Preparation** – All samples are to be prepared according to Spectroscopy's *Sample Preparation SOP 501*. Batch #'s are assigned by this section. All batches are numbered with reference to protocol, month, date, and year (i.e. PRE010108 reflects a

Pretreatment batch prepared on January 1st, 2008). Prepared batches are recorded in the *Furnace Batch Log* (See section 15.0).

9.2. **Instrument Setup**

9.2.1. **Changing Technique on AAnalyst 800-** Before you change the technique from Furnace to Flame or vice versa, switch off EDL's. When you have changed the technique, make sure that the lamp current is set correctly in the *Lamps* window. This option is not available on AAnalyst 600.

9.2.2. **Setting up the Furnace System**

9.2.2.1. Make sure fume ventilation system is operating.

9.2.2.2. Turn on the gas supply. Argon pressure at 51-58 psig is needed for operation (*PE THGA Users Guide*, pg 5-18).

9.2.2.3. Make sure that the flame guard is removed (Analyst 800 only) and that the Furnace Auto-sampler is in position and is locked into place.

9.2.2.4. Switch on the computer and printer.

9.2.2.5. Switch on the spectrometer.

9.2.2.6. Start AA WinLab: On the *Taskbar*, click on *Start* then on *Programs> {Spectrometer name} > AA WinLab Analyst.*

9.2.2.7. On the *Toolbar*, click on *Technique* and select the appropriate technique (Select Furnace on Analyst 800 only).

9.2.2.8. Check the graphite tube, contact rings and probe alignment (Sections 3-10 to 3-17 in the PE THGA Graphite Furnace manual for the Tube and Contact Rings, and for the Probe Alignment, in the Furnace Control Window, click on *Align Tip* and make the appropriate choices).

9.2.3. **Install Lamps-** Ensure that the proper identification plug is inserted for the EDL lamps and that the current applied is listed properly in the Method.

9.2.3.1. Install the lamps in the lamp compartment.

9.2.3.2. On the Toolbar, click on Lamps. The Lamps window appears.

9.2.3.3. Insert the desired lamps (The quartz or glass bulb end of the lamp must face the Zeeman module). Note: EDL lamps must be used with their corresponding ID pins.

9.2.3.4. Check the energy of each lamp before beginning an analysis. The energy is shown by the bar graph and the Energy value.

9.2.3.5. Close the Lamps window.

9.3. **Inserting and Conditioning the Graphite Tube-** Refer to *PE THGA Graphite Furnace Users Guide*, pp. 3-12, 3-13 when inserting a graphite tube. When installing a new graphite tube, perform the procedure to condition the graphite tube outlined on page 3-17. When inserting a previously conditioned graphite tube follow the procedure to remove contamination on page 3-18.

9.4. **Autosampler alignment** – Alignment is performed when contact rings are replaced or as needed. Select the *Furnace* toolbar and select *AlignTip* for these options. The *Align Autosampler Tip Wizard* window appears and based on the task selected, the wizard will guide you through the procedures discussed below. The user may also refer to the online Help in the AA WinLab program for instructions.

The autosampler probe must be aligned to ensure that the delicate tip of the sampling pipette enters the sample injection hole in the graphite tube without striking the edge of the hole. The pipette tip should not strike the integrated platform. Proper alignment of 1-2 mm above the platform will also ensure that the measurement solution is correctly dispensed. Refer to PE THGA Graphite Furnace Users Guide, pp 2-17 – 2-19 for alignment procedure. To check the penetration depth of the autosampler in the graphite tube, refer to pp 2-19 – 2-20. To adjust the immersion depth of the pipette tip in the sample cup, refer to page 2-21.

9.5. **Sample Analysis Procedure** (Refer to the *PE AA WinLAb Software Guide* for software details).

9.5.1. Create a method if a method for a particular element has not yet been created.

9.5.2. Set up the calibration pages for the calibration technique intended for use.

9.5.3. Allow the lamps to warm up until the lamp energy remains stable.

9.5.4. Select *Wrkspc* from the toolbar. Select the appropriate *Furnace Workspace* file. Three windows appear: 1) *An Automated Analysis Control* window 2) *Calibration Display* window 3) *Results* window.

9.5.5. Open Method: Choose a method from the *Automated Analysis* window by double clicking on the *Method* space **or** from the toolbar, select *File →Open Method.* Highlight the appropriate method and select *OK*.

9.5.6. Create a Sample Information File: The entries in the sample information file depend on calibration technique that you intend to use. From the toolbar, select *File → New→ Sample Info File*. Select the *Default design*. The *Sample Information Editor Window* appears. Enter the sample location IDs under *ALS Location*. Enter the Sample ID's under *Sample ID*. The user may enter any applicable dilutions in this window and the software will factor these calculations into the final results. Enter the File name under *Batch ID*. From the toolbar, select *File →Save As →Sample Info File*. Type in the File name (Batch ID). Select *Save*. The user may also select *File→ Print→ Active Window* to print the Sample Info file.

9.5.7. Prepare the autosampler with samples, QC and check samples, calibration solutions and matrix modifiers. The sample tray corresponds to the ID/WT file that has been set up for each batch. In the AZ position place a sample cup with 1% HNO3. Place standards and matrix modifiers according to element set-up. Samples begin in position one. Place cover on autosampler.

9.5.8. Perform an automated analysis: In the *Automated Analysis Control* window, under the *setup* tab, select *Open Results Data Set*. Enter in the file name and select *OK*. Ensure that the *sample info file* matches the *results data set* in the *Automated Analysis Control* window. Select the *Analyze* tab from this window and the following options to begin analysis appear: *Analyze All*, *Calibrate, Analyze Samples*, and *Reset Sequence*. Refer to *PE AA Winlab Software Users Guide*, pp. 9-7 – 9-18 for further automated analysis details.

- *Analyze All* - The user can create a new calibration curve and begin analysis. The system analyzes the calibration solutions first, immediately followed by the samples and any other solutions i.e. QC and check samples.
- *Calibrate* – Selecting this function allows the user to analyze the calibration solutions generating a calibration curve. If satisfied with the calibration, the calibration check samples and samples can then be analyzed by clicking on *Analyze Samples*.
- *Analyze Samples* – A calibration curve must appear in *Calibration Display* window for the *Analyze Samples* function to operate. (Note: A preexisting calibration curve may be

selected from the *Analysis* toolbar →*Recall Calibration* when *Analyze Samples* is chosen).

- *Reset Sequence*- This option allows the analytical sequence to be reset to the beginning when the sequence has been interrupted. The next analysis will begin with the first sample in the list.

9.6. Stopping an analysis

9.6.1. In the Automated Analysis window click on the button you used to start the analysis. i.e. *Analyze Blank, Calibrate,* or *Analyze Samples.* The *Stopping an Analytical Sequence* dialog appears.

9.6.2. Use this dialog to tell the system exactly which solutions to analyze before it stops or click on *Cancel* to continue the analysis where you interrupted it.

9.7. Restarting an analysis

9.7.1. To restart the analysis from the beginning:

1. *Stop* the analysis.
2. Use the dialog to tell the system exactly which solutions to analyze before it stops.
3. In the *Automated Analysis* window, click on *Reset.*
4. Restart the analysis.

To continue the analysis where you interrupted it or to continue with a specific sample:

1. *Stop* the analysis.
2. The *Continuing an Analytical Sequence* dialog appears.
3. Use this dialog to tell the system exactly which solution to start the analysis with.

9.8. **Recalibration and Reslope**- The user defines the type and frequency of automatic recalibrations and reslopes on the *Checks page* of the *Method Editor.* To perform a recalibration:

1. Stop the analysis.
2. In the *Automated Analysis* window, click on *Reset...*
3. In the *Automated Analysis* window, click on *Calibrate.*

9.9. **Shutting down-** Turn off all lamps. Right click on *file.* Scroll down and click on *exit.* Answer any prompts. When you have exited the Winlab software you may then shut down the computer,printer, and spectrometer.

10.0 DATA REPORTING

10.1. **Calculations** – All data is reported in µg/L, except for sludge and solid samples which require units of mg/Kg. Ensure that the ID file contains the appropriate dilution and weight factors.

10.1.1. **Dilution and Concentration factors-** Use the following equation:

$$\text{Result} \times \frac{\text{Final Sample Volume}}{\text{Original sample Volume}}$$

Dilution factor: $\frac{\text{Final Sample Volume}}{\text{Original sample volume}}$ $\frac{\text{(10 ml sample + 40 ml DI/RO water)}}{\text{10 ml}} = 5X$

Concentration factor: $\frac{\text{Final Sample Volume}}{\text{Original Sample Volume}}$ $\frac{\text{25 ml}}{\text{250 ml}} = 0.10X$

10.1.2. **Conversion of µg/L → mg/Kg:**

$$\frac{(\text{mg/L})(\text{Final Volume ml})}{(\text{wt. grams})} \times \text{Dilution Factor (2)} = \text{mg/Kg} \quad \text{--- or---}$$

$$\frac{(\mu\text{g/L})(\text{Final Volume ml})}{(\text{wt grams})\ 1000} \times \text{Dilution Factor (2)} = \text{mg/Kg}$$

10.2. **Logbook Entry** –Data is not recorded in a logbook. All data is generated through the WinLab software in a report format. Ensure that the sample info file matches the results data set name.

1. Generate a report after all the data has been collected.
2. Utilize the *Data Manager* for report generation.
3. Staple a copy of the ID file, report, and raw data.
4. Once calculations are finished, place the report/data in appropriate files.

10.3. **Corrective Actions**- Follow requirements in QA SOP-003 and QA SOP-005. The Corrective Actions section covers the following topics: 1) Out of Control Data Procedures and 2) Corrective Action Logbooks. (See section 15.0 for *Furnace Maintenance, Repair & Corrective Actions Logbook*).

10.4. **Data Assessments** – Follow requirements in QA SOP-005. The Data Assessments section covers the following topics: 1) Accuracy and Precision 2) Data Validation Procedures 3) Data Reporting Procedures.

10.5. **Data Entry** – Enter results in SQL-LIMS as required.

11.0 **MAINTENANCE-** Routine maintenance is required to ensure the highest possible level of performance. For details consult *PE THGA Graphite Furnace Users Guide*, section 3 and *PE AAnalyst 600 Users Guide*, section 4. All servicing should be performed by a Perkin Elmer service representative. Document all maintenance procedures in the appropriate *Furnace Maintenance, Repair, and Corrective Actions Logbook.* (See section 15.0).

11.1. **Daily Maintenance**

11.1.1. **Graphite tube**- Check the graphite tube for deposits around the injection hole or on the integrated platform. Install a new tube if contact surfaces on the tube are pitted or cracked. For cleaning procedure, refer to *PE THGA Graphite Furnace Users Guide*, pg. 3-14.

11.1.2. **Argon Supply**- Ensure that an adequate supply of argon is available and connected to the system. Argon output pressure: 51-58 psig. For detailed gas requirements, refer to the *Technical Data* section, *PE THGA Graphite Furnace Users Guide*, pg. 5-18.

11.1.3. **Lamp Energy**- Check the stability of the lamp energy prior to analysis. The HCL lamps take approximately 20 mins to warm up and stabilize and the EDL lamps take approximately an hour to warm up and stabilize. Check by noting the lamp energy over time after the warm up period.

11.1.4. **Exhaust Ventilation**- Check that the vent is on and drawing air

11.2. **General Maintenance-** The amount and type of samples analyzed will dictate how often general maintenance procedures should be performed.

11.2.1. **Furnace Assembly**- Clean the furnace assembly

11.2.2. **Furnace Windows**- Clean the quartz and side windows periodically. Cleaning frequency depends on the type of samples being analyzed. The cleaning procedure is in *PE THGA Graphite Furnace Users Guide*, pg. 3-32.

11.2.3. **Autosampler**- Wipe over the external surface of the autosampler with a lint free cloth moistened with a dilute solution of laboratory detergent.

11.2.4. **1% HNO_3 Reservoir**- Ensure that the reservoir is filled with 1% HNO_3.

11.2.5. **Waste Bottle**- Regularly check the waste bottle and empty it periodically. Never allow it to overflow.

11.2.6. **Contact Rings**- Check the contact rings for wear. If they are pitted or cracked, install new ones. For installation procedure, refer to *PE THGA Graphite Furnace Users Guide*, pg. 3-32.

11.2.7. **Autosampler Probe**- Replace the autosampler probe as needed. Ensure that all tubes are clean and free from kinks. Change any tubes that may be damaged or contaminated. Check the pipette tip on the probe and ensure it is not damaged. Repair the tip or install a new probe if needed. See *PE THGA Graphite Furnace Users Guide*, pg 3-47.

11.2.8. **Air Filter**- Replace or clean the air filter located in the back of the instrument as needed. To clean, vacuum or rinse the filter with deionized water. To replace, refer to *PE AAnalyst 600 Users Guide*, pg 4-10.

11.3. **Perkin Elmer Preventive Maintenance visit-** At least annually, the following preventive maintenance is performed by a service engineer from Perkin Elmer:

1. Optics cleaned and inspected
2. Sensitivity Checked
3. Wavelength checked
4. Mechanical assembly cleaned
5. Cooling System checked

12.0 TROUBLESHOOTING

12.1. Refer to the *THGA Graphite Furnace Techniques and Recommended Conditions* (pp. 5-1 – 5-10) manual for troubleshooting concerning the following topics:

1. Signal is too low/high; m_0 is too low/high
2. The baseline has shifted upward or noise has increased
3. Very high blank observed during a dry run
4. An increase in the background signal observed during the run of several replicates
5. Multiple Peaks
6. Precision is poor or becoming poorer
7. Rapid corrosion of tube in absence of pipetted sample
8. Rapid corrosion to left or right of injection hole with pipette sample

12.2. Table 3& 4 cover typical problems encountered with the PE THGA Graphite Furnace. For Spectrometer, Computer, Furnace and Furnace Autosampler, and Furnace technique Analyses detailed troubleshooting, refer to the *PE AA WinLab Analysis Systems Troubleshooting* guide.

Table 3. Spectrometer Troubleshooting

Problem	Possible Cause	Remedy
Hallow Cathode lamp will not light	Spectrometer is off Lamp or turret not plugged Insufficient current to lamp	Turn spectrometer on Connect lamp or turret Use Align Lamps to set the proper current
EDL will not light	EDL power supply not on Need light source to initiate	Turn on power supply Use igniter to turn on
Lamp Energy too Low or Fluctuating	Lamp starting to deteriorate Insufficient current to lamp Wrong entries in the Align Lamps window Dirty windows Beam Obstruction	Warm up lamp 30 – 60 min. or replace lamp Use Align Lamps to set the proper current Clean the lamp end, furnace or atomizer compartment windows as described in the user's guide Remove obstruction in either the graphite tube or atomizer compartment
Computer unable to find proper Lamp	Lamp out of alignment Lamp not coded	Check recommended settings under Select Elements

Table 4. Graphite Furnace Troubleshooting

Problem	Possible Cause	Remedy
Graphite furnace fails to operate	Furnace not plugged in Gas pressure not in range Graphite tube not installed or is defective	Check power source, connections, increase inert gas pressure Install and align a graphite tube
Furnace overheats	Insufficient cooling water flow	Verify cooling water flow (2.5 L/min)
Suspicious analytical results	Contaminated contact cylinders	Change contact cylinders or change graphite tube
Analytical result too high	Contaminated contact cylinders Contaminated graphite tube	Change graphite tube
Background signal increases suddenly during run	Block gas passages in contact cylinder	Change cylinders
High tube impedance error	Defective tube Eroded contact cylinders	Change graphite tube
High dry temperature required	Poor contact between contact cylinder and graphite tube	Clean contact cylinders
Pretreatment temperature too high	Can cause analyte loss prior to atomization	Re-determine proper temperature for analyte in current sample matrix
Rapid corrosion of tube	Low argon flow rate Inadequate drying step.	Adjust flow rates in the program See Recommended Conditions to adjust program in the Method editor

13.0 WASTE DISPOSAL AND POLLUTION PREVENTION

13.1. All waste disposal procedures will follow the Water Quality Laboratory CHP (Section 5.12-Revision December 2005). Disposal procedure is as follows:

13.1.1. Discard all remaining analyzed samples in an acid sink.

13.1.2. All sample labware must be washed with laboratory soap inside and out followed by multiple rinses with distilled or deionized water.

13.2. Pollution Prevention - Eliminate waste at the source and base the quantity of purchased reagents on expected usage during their shelf life.

14.0 REFERENCES

14.1. American Public Health Association, American Water Works Association, and Water Environment Federation. 1995. 19th ed. *Standard Methods for the Examination of Water and Wastewater*: Method 3113 B, Electro thermal Atomic Absorption Spectrometric Method. APHA, Washington DC.

14.2. EPA Method 200.9 Determination of Trace Elements by Graphite Furnace Atomic Absorption.

14.3. Perkin Elmer 1998-2000. *AAnalyst 600 Atomic Absorption Spectrometer Users Guide*. Shelton, Connecticut.

14.4. Perkin Elmer 1991-1999. *The THGA Graphite Furnace Techniques and Recommended Conditions*. Ueberlingen, Federal Republic of Germany.

14.5. Perkin Elmer 1998-2000. THGA Graphite Furnace Including the AS-800 Autosampler Users Guide. Shelton, Connecticut.

14.6. Perkin Elmer 1996. AA WinLab Software Guide. USA.

14.7. Perkin Elmer 2003. Cooling System for Atomic Spectrometry Systems User's Guide. Shelton, Connecticut.

14.8. Perkin Elmer 1999-2001. THGA *Furnace Graphite Contact Tools User's Guide*. Shelton, Connecticut.

14.9. Perkin Elmer 1998. *AA WinLab Analysis Systems Troubleshooting*. Bodenseewerk. Federal Republic of Germany.

14.10. Metals Sample Preparation SOP 501.

15.0 LOGBOOK CONTROL DOCUMENTS

Title
Furnace Standards Logbook
Furnace Instrument and Sample Control Logbook (AA600-1, AA600-2, AA800)*
Furnace MDL Verification (AA600-1, AA600-2, AA800)*
Furnace Maintenance, Repair, & Corrective Actions Logbook (AA600-1, AA600-2, AA800)*
HNO_3 Preparation Logbook/HNO_3 & DI H_20 Quality Control
Furnace Batch Log
There are three logbooks designated for each Graphite Furnace: 1. AA600-1, Serial # 600S6080103 2. AA600-2, Serial # 600S704040 3. AA800, Serial # 8257